

Docket No.: 1155-0214P  
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:  
Mamoru TAKAHASHI et al.

Application No.: 09/744,904

Confirmation No.: 8530

Filed: January 31, 2001

Art Unit: 1713

For: ETHYLENE (CO)POLYMERS AND USES  
THEREOF

Examiner: R. A. Lee

DECLARATION UNDER 37 C.F.R. 1.132

MS AF  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

I, Naoto MATSUKAWA, declare the following:

I received my degree of M.A. in 1997 from Okayama University, Faculty of Engineering,  
Department of Applied Chemistry.

I joined Mitsui Petrochemical Industries (now Mitsui Chemicals, Inc.) in 1997.

Since 1998, I have been an olefin polymerization catalysis researcher at Sodegaura  
research center.

I am one of the inventors of the present invention.

I have read and understand the Office Action dated March 23, 2007 and the reference  
cited therein to Malmberg et al. (Macromolecules, 1998, Vol. 31, pages 8448-8454).

Currently, claim 1 recites that the inventive ethylene (co) polymer (A1) which is either  
an ethylene homopolymer or a copolymer of ethylene and an  $\alpha$ -olefin of 4 to 20 carbon atoms,  
comprises the following Features: (iv<sub>A1</sub>)<sup>1</sup> the number of branches having a length equivalent to

<sup>1</sup> I use herein, the numbering of the Features as used in the claims.

that of hexyl or longer measured by  $^{13}\text{C}$ -NMR is less than 0.1 per 1,000 of carbon atoms, and ( $v_{A1}$ ) the intrinsic viscosity  $[\eta]$  in dl/g measured at 135°C in decalin and the melt flow rate MFR in g/10 minutes measured under 2.16 kg load at 190°C satisfy the following relations:

$$[\eta] > 1.85 \times \text{MFR}^{-0.192} \text{ when MFR} < 1, \text{ and}$$

$$[\eta] > 1.85 \times \text{MFR}^{-0.213} \text{ when MFR} \geq 1.$$

I have performed the following experiment(s) to determine that none of the polymers of Malmberg et al. have this combination of Features ( $iv_{A1}$ ) and ( $v_{A1}$ ).

Sample B5 is discussed at page 8450, 2<sup>nd</sup> column, lines 5-6 from bottom of Malmberg et al., and is the only example wherein the amount of branching is described. Accordingly, it is my opinion that only Sample B5 of Malmberg et al. could meet the branching Feature ( $iv_{A1}$ ) of claim 1.

I now describe the process I used for repeating Sample B5 of Malmberg et al. and report that Sample B5 does not meet the MFR and intrinsic viscosity  $[\eta]$  relationship described in Feature ( $v_{A1}$ ) of claim 1. The experiments disclosed herein were performed by me or under my direct supervision.

Sample B5 disclosed in Malmberg et al. has been essentially repeated according to the description of Malmberg et al, which is as follows:

#### Experimental Section

Polymerization method: solution polymerization

Solvent: Toluene 800ml

Ethylene partial pressure: 1 bar

Catalyst: Ethylene bis indenyl zirconium dichloride (Not supported, dissolved in Toluene)

Co-catalyst: Methyl Alumoxane (MAO)

Comonomer: none

Hydrogen: not added

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**Table 1 : Polymerization conditions**

Sample	Catalyst: mM	Co- catalyst: mM	Ethylene Flow rate: L/hr	Polymerization Temperature:	Polymerization Time: min.	Yield: g
Run #1	0.0008	4.0	100	80	5	6.51
Run #2	0.0008	4.0	100	80	5	6.84

**Table 2 : Physical Properties Of Polymer Obtained**

Sample	Mn	Mw	Mw/Mn	$[\eta]$ : dg/l	MFR	*1
Run #1	$3.32 \times 10^4$	$6.68 \times 10^4$	2.0	1.44	1.70	1.652
Run #2	$3.45 \times 10^4$	$6.87 \times 10^4$	2.0	1.52	1.09	1.816

\*1 =  $1.85 \times \text{MFR}^{0.213}$ **Condition of GPC measurement**

Equipment: Gel Permeation Chromatograph, Product of Waters Corporation  
Alliance GPC 2000 series

Measurement condition:

Column: Product of Tosoh Corporation

TSKgel GMH6-HTX2 + TSKgel GMH6-HTX2

(Column size: 7.5 mm I.D. x 30 mm)

Column Temperature: 140°C

Mobile phase: o-dichlorobenzene [containing 0.025% of BHT (Butyl Hydroxy Toluene)]

Detector: differential refractometer

Flow rate: 1 mL/min.

Concentration at testing: 0.15% (W/V)

Injection volume: 500 $\mu$ L

Time interval of sampling: 1 sec.

Calibration sample: mono-dispersed polystyrene (product of Tosoh Corporation)

**Condition of MFR measurement**

2.16 Kg load at 190°C

**Condition of  $[\eta]$  measurement**

Measured in decalin at 135°C

### Comments/Conclusions Based on Experimental Results

As shown in Table 2, the MFR and intrinsic viscosity  $[\eta]$  relationship described in Feature (v<sub>A1</sub>) of claim 1 is not satisfied, i.e., Sample B5 of Malmberg et al. does not meet the requirement of  $[\eta] > 1.85 \times \text{MFR}^{-0.213}$  when  $\text{MFR} \geq 1$ .

I am aware that the polymerization time used herein is different from that described for the sample disclosed in Malmberg et al. Specifically, the polymerization time of the experiment (5 minutes) is different from that of Malmberg et al. (60 minutes). However, for the following technical reasons, it is my opinion that the difference in polymerization time would not significantly affect the ratio of intrinsic viscosity  $[\eta]$  and  $\text{MFR}^{-0.213}$ .

The polymer of Malmberg et al. is obtained by polymerizing olefins using a metallocene catalyst. The mechanism of the olefin polymerization is called an addition polymerization. The mechanism is described in "Chemistry of polymer synthesis," revised version (published by KAGAKUDOJIN in March 1, 1989, 11th impression of the second edition), a copy of which is attached hereto for the Examiner's convenience. The relevant part (pages 33 to 34) of which is translated to English as follows.

Among these reactions addition polymerization and polycondensation have been studied from long ago, and it is believed that addition polymerization and polycondensation proceed with chain reaction and stepwise reaction, respectively. ...

Chain reaction and stepwise reaction have essentially different polymerization mechanisms.

Generally, chain reaction comprise following 4 primary reactions:

initiation that generates unstable chain carrier,

propagation in which chain carrier react in cascade,

termination in which propagation is terminated, and chain transfer reaction.

Supposing that M stands for monomer, P stands for polymer, and A stands for substance that can cause chain transfer reaction; each reaction can be described as follows:

Initiation:  $M \rightarrow M^*$

Propagation:  $M_n \rightarrow M_n^*$

Termination:  $M_n \rightarrow P$

Chain transfer:  $M_n^* + A \rightarrow P + A^*$

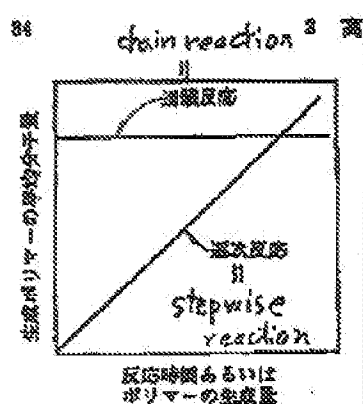
wherein  $M_n^*$  is the chain carrier and any of radical, anion or cation. Among these primary reactions, Initiation is the slowest one, and once a chain carrier is generated, propagation occurs immediately.

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Generally, when polymerization proceeds with chain reaction, average molecular weight of the resultant polymer is constant as in figure 2-1, regardless of time of reaction. To the contrary, in stepwise reaction functional group react consecutively to form polymer. There are no unstable intermediates such as chain carrier in the reaction, and average molecular weight of the polymer increase with time of reaction as in figure 2-1.

Figure 2-1



[caption]

Relation between average molecular weight of the polymer and time of reaction for chain reaction and stepwise reaction

[Y-axis]

average molecular weight of polymer

[X-axis]

time of polymerization reaction

This teaching can be summarized follows.

With respect to polymerization, there are chain reactions and stepwise reactions. In the case of addition polymerization, the reaction proceeds with chain reaction. The average molecular weight is constant regardless of polymerization time.

So the polymer properties such as MFR and intrinsic viscosity, which are closely related to the molecular weight of a polymer, are not expected to change with time. As such, it is my opinion that the difference in polymerization time between Sample B5 of Malmberg et al. and the polymerization time reported herein would not significantly affect the ratio of intrinsic viscosity  $[\eta]$  and  $MFR^{-0.213}$ .

In a *separate matter*, the Examiner expressed during the recent Interview with my representative, Dr. Dahlen, that the ratio of catalyst to cocatalyst is an important variable. The Examiner is aware that Malmberg et al. do not disclose the ratio of catalyst/cocatalyst. The Examiner is concerned that the catalyst/cocatalyst ratio affects the MFR and intrinsic viscosity  $[\eta]$  of the Sample B5. I respectfully disagree with the Examiner.

First, if the ratio of catalyst/co-catalyst greatly affects the properties of the polymer produced, then it makes sense that Malmberg et al. have not placed into possession of the public the polymer of Sample B5. In other words, based on this logic, if the ratio is not disclosed, then Sample B5 of Malmberg et al. could not be reproduced.

Second, I conducted the experiments to show that Sample B5 does not satisfy the equation regarding MFR and  $[\eta]$  of the present claim, believing that the effect of the co-catalyst/catalyst ratio is small. It is my opinion that the experiments described herein are sufficient to show that the Sample B5 does not satisfy the relation of the claim regarding MFR and  $[\eta]$ .

It is my opinion that since the polymerization conditions are not disclosed in Malmberg et al., it is logical to assume that the polymerization conditions are in the normal range that one skilled in the art would select. As such, there is not a big difference between the polymerization conditions of the experiments described herein and that of Malmberg et al.

In conclusion, it is my opinion that none of the polymers of Malmberg et al. have the inventive combination of Features (iv<sub>A1</sub>) and (v<sub>A1</sub>).

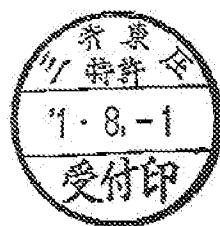
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated: August 21, 2007By Naoto Matsukawa  
Naoto Matsukawa

Attached: "Chemistry of polymer synthesis," revised version (published by KAGAKUDOJIN in March 1, 1989, 11th impression of the second edition).



改訂 高分子合成の化学

著 行 隆 津 大

化学同人



## 2.3 高分子合成反応の分類と特徴

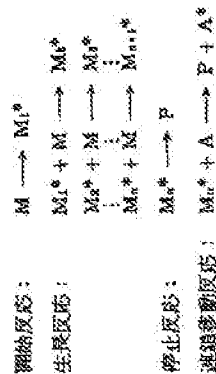
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離する場合や脱水果を起しながらかち重なる場合であり、水やアルコールなどが脱離する重縮合と機構的に異なる点が多い。本書では区別して取り扱うことにする。

このなかで、付加重合および重縮合は古くから詳しく研究され、それぞれ連鎖反応(chain reaction)および逐次反応(stepwise reaction)で進むと考えられている。そのほかの反応は明らかでない場合もあるが、1~4は連鎖反応で、5~8は逐次反応で進むとみられている。

連鎖反応ならびに逐次反応による高分子の生成反応は、本質的に異なった特徴を示す(表2-2参照)。一般に、連鎖反応は次の四つの素反応からなっている。すなわち、不安定な連鎖で伝播(chain carrier)のできる開始反応(initiation)、それが次々に反応を続ける生長反応(propagation)、それが消失する停止反応(termination)、およびそれが他の物質に移動する連鎖移動反応(chain transfer reaction)である。

いま、 $M$ をモノマー、 $P$ をポリマー、 $A$ を連鎖移動反応を起すような物質とすると、次のように書ける。



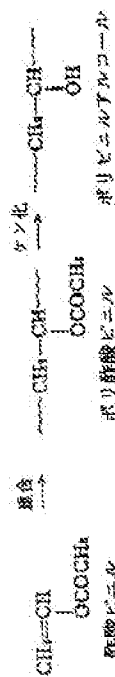
ここで、 $M_n^*$ は連鎖でい伝体で、ラジカル、カチオン、アニオンの3種類がある。ラジカルを生成して進む重縮合では、これら素反応のうちで、開始反応が最も起こりにくく、一度連鎖でい伝体が生成するときわめてすみやかに生長する。一般に、連鎖重縮合で進む場合は図2-1に示すように生成ポリマーの平均分子量は反応時間に無関係に一定である\*。

\* 図2-1の図解はラジカル重縮合で、しかも重合初期の段階で成立する。重合がかなり進行した場合やイオン重縮合では成立しない(分子量が增大する)場合がある。また、リビング重縮合では分子量は重合率とともに増大する。

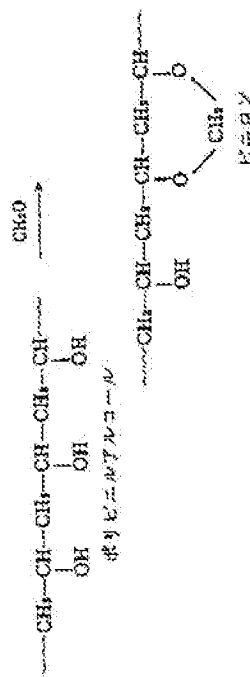
## 2 高分子合成の基礎

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重合によって生成するはずであるが、ビニルアルコールは実在しない(アセトアルデヒド異性体として存在する)。したがって、次のように酢酸ビニルを重合してポリ酢酸ビニルをつくり、ついでケン化することによって初めて合成される。



また、ビニロン繊維はポリビニルアルコール糸にホルムアルデヒドを反応させ、部分的にホルマル化したものである。



このように高分子の化学反応によっても、多くの重要な高分子が合成され、また高分子の性質の改善(改質)が行われている(14章参照)。

## 2.3 高分子合成反応の分類と特徴

以上に述べた考察から、高分子から高分子を合成する反応を分類すると次のようになる。

1. 付加重合(重合)
2. 環化重合
3. 異性化重合
4. 開環重合
5. 脱離重合
6. 重付加
7. 重縮合
8. 付加縮合

この分類は、脱離重合を除いては多くの書物にみられる分類と同じである。ここでいう脱離重合は窒素、二硫化炭素などの気体が重合に伴って脱

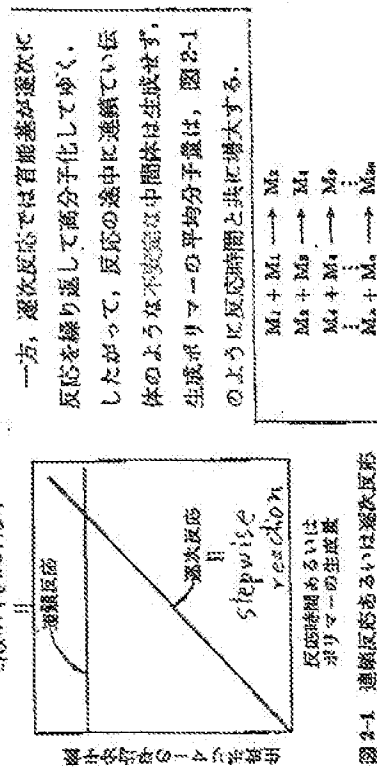


図 2-1 連鎖反応による高分子生成反応における反応時間と平均分子数の関係 (いずれも反応初期を示したもので反応後期には増大する)

連鎖反応および逐次反応による高分子化反応の典型的な違いを表 2-2 にまとめると、

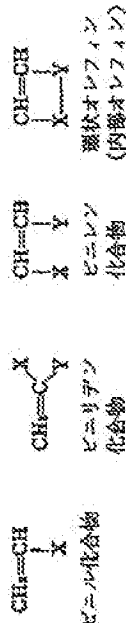
表 2-2 連鎖反応と逐次反応による高分子合成反応の比較

連鎖反応による高分子化(付加重合)	逐次反応による高分子化(逐次重合)
生長は連鎖でい伝体とモノマーの反応で起こり、連鎖でい伝体と容易に反応する物質を少量加えると重合反応は完全に止まる。	モノマーあるいはポリマー中の官能基どうしの反応で起こり、1 官能基性化合物を加えると分子量は低下する。
モノマー濃度は反応を通じて漸次減少し、反応の途中では常にモノマーとポリマーの混合物である。	モノマー濃度はすみやかに減少する。重合度が 10 となると、モノマー濃度は 1% 以下となる。
高分子量のポリマーがただちに生成し、反応の進行と共に分子量は原則として変化しない(図 2-1)。	分子量は反応の進行と共に増大(図 2-1)し、高分子量のポリマーを得るには長時間を要する。

## 2.4 ビニル化合物の重合

### 2.4.1 ビニル化合物の重合の形式

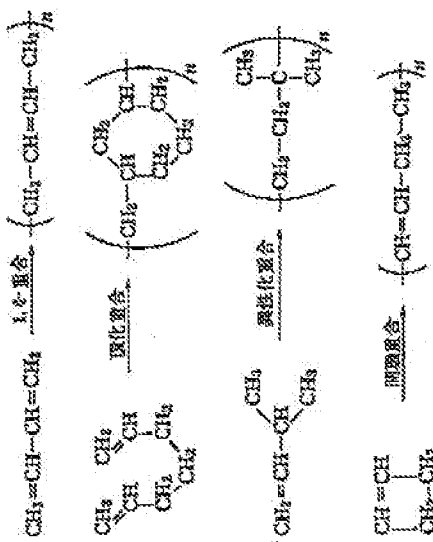
炭素-炭素二重結合を有する化合物は、それと結合した置換基の数と付加によって次のようによばれる。



このうち、単独重合するモノマーは主としてビニルとビニリデン化合物であるので、このような化合物を総称してビニルモノマー (vinyl monomer) と区別せずによばれることがある。これら化合物は、それぞれ重合のしやすさは異なるが、一般に、二重結合が単に開いて付加重合する。



このような重合の形式はビニル重合 (vinyl polymerization) とよばれる。ただし、ある種のビニルモノマーでは上述のビニル重合と同時に、次のような形式の重合が起こる。



このうち、共役ジエンの 1,4-重合を除いては 9 章で述べることにする。ビニル重合は連鎖反応で進むので、連鎖でい伝体がラジカルであるか、カチオンであるか、アニオンであるかによって、それぞれラジカル重合 (radical polymerization)、カチオン重合 (cationic polymerization)、あ

連鎖移動定数	84, 143
連鎖移動反応	93, 154
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連鎖反応による高分子合成反応	33

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